

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

Mo-6397/LeA 33,477

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

09/868489
To Be AssignedTRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/09689	December 9, 1999	December 21, 1998

TITLE OF INVENTION LIQUID TETRABUTYL AMMONIUM PHENOLATE FORMULATION

APPLICANT(S) FOR DO/EO/US HESSE, Carsten; JANSEN, Ursula and RECHNER, Johann

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. is attached hereto (required only if not communicated by the International Bureau).
 - b. has been communicated by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. is attached hereto.
 - b. has been previously submitted under 35 U.S.C. 154(d)(4).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. are attached hereto (required only if not communicated by the International Bureau).
 - b. have been communicated by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
8. An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A FIRST preliminary amendment.
14. A SECOND or SUBSEQUENT preliminary amendment.
15. A substitute specification.
16. A change of power of attorney and/or address letter.
17. A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. Other items or information:

Abstract

U.S. APPLICATION NO. (if known, see 37 CFR 1.55)
To Be Assigned **09/868489**INTERNATIONAL APPLICATION NO.
PCT/EP99/09689ATTORNEY'S DOCKET NUMBER
Mo-6397/LeA 33,47721. The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 860.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than 20 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	9 -20 =	0	x \$18.00	\$ 0.00
Independent claims	4 -3 =	1	x \$80.00	\$ 80.00
TRIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00

09/868489

JC18 Rec'd PCT/PTO 18 JUN 2001

PATENT APPLICATION
Mo-6397
LeA 33,477

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
CARSTEN HESSE ET AL) PCT/EP 99/09689
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: LIQUID TETRABUTYL AMMONIUM)
PHENOLATE FORMULATION)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to its examination, kindly amend the English language translation of the enclosed application as follows:

"Express Mail" mailing label number ET146895025US
Date of Deposit June 18, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Dorothy P. Colangelo
(Name of person mailing paper or fee)
Dorothy P. Colangelo
Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Delete the Title of the application - appearing in page 1 - and insert therefor:
-- Liquid Tetrabutyl Ammonium Phenolate Formulation --.

Please insert the following Abstract page:

-- LIQUID TETRABUTYL AMMONIUM PHENOLATE FORMULATION

ABSTRACT OF THE DISCLOSURE

A process for preparing a formulation containing tetrabutylammonium phenolate and phenol is disclosed. The process entails combining a solution of tetrabutylammonium bromide in phenol with a solution of sodium phenolate to form a mixture, excess phenol is removed by distillation, and sodium bromide is filtered off. The formulation, that contains tetrabutylammonium phenolate and phenol in a weight ratio of 40:60 to 70:30, has a solidification point of less than 25°C. and finds use as a catalyst constituent. --

IN THE CLAIMS:

Please cancel Claim 5.

Please add the following claims:

--6. A process for preparing a formulation containing tetrabutylammonium phenolate and phenol comprising combining a solution of tetrabutylammonium bromide in phenol with a solution of sodium phenolate in phenol to form a mixture, removing from the mixture excess phenol by distillation, and filtering off sodium bromide, said tetrabutylammonium phenolate and phenol being present in said formulation in a weight ratio of 40:60 to 70:30, said formulation having a solidification point of less than 25°C.

7. A process for preparing a formulation containing tetrabutylammonium phenolate and phenol comprising combining a solution of tetrabutylammonium bromide in phenol with an aqueous solution of sodium phenolate to form a mixture, removing from the mixture water and excess phenol by distillation, and filtering off sodium bromide, said tetrabutylammonium phenolate and phenol being present in said

formulation in a weight ratio of 40:60 to 70:30, said formulation having a solidification point of less than 25°C.

8. A process for preparing a formulation containing tetrabutylammonium phenolate and phenol comprising combining a solution of tetrabutylammonium bromide in phenol with a solution of sodium phenolate trihydrate in phenol to form a mixture, removing from the mixture water and excess phenol by distillation, and filtering off sodium bromide, said tetrabutylammonium phenolate and phenol being present in said formulation in a weight ratio of 40:60 to 70:30, said formulation having a solidification point of less than 25°C.

9. The formulation prepared by the process of Claim 6.

10. A method of using the formulation of Claim 9 comprising preparing a catalyst. --

REMARKS

The present amendment seeks to place the application in better conformance with U.S. practice. A page containing an Abstract of the disclosure is enclosed.

Entry of the amendment is requested.

Respectfully submitted,

CARSTEN HESSE
URSULA JANSEN
JOHANN RECHNER

By _____


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Mo-6399
LeA 33,477

Version with markings to show changes

IN THE SPECIFICATION:

Delete the Title of the application - appearing in page 1 - and insert therefor:
-- Liquid Tetrabutyl Ammonium Phenolate Formulation --.

Please insert the following Abstract page:

--
LIQUID TETRABUTYL AMMONIUM PHENOLATE FORMULATION

ABSTRACT OF THE DISCLOSURE

A process for preparing a formulation containing tetrabutylammonium phenolate and phenol is disclosed. The process entails combining a solution of tetrabutylammonium bromide in phenol with a solution of sodium phenolate to form a mixture, excess phenol is removed by distillation, and sodium bromide is filtered off. The formulation, that contains tetrabutylammonium phenolate and phenol in a weight ratio of 40:60 to 70:30, has a solidification point of less than 25°C. and finds use as a catalyst constituent. --

IN THE CLAIMS:

Please cancel Claim 5.

Please add the following claims:

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7. A process for preparing a formulation containing tetrabutylammonium phenolate and phenol comprising combining a solution of tetrabutylammonium bromide in phenol with an aqueous solution of sodium phenolate to form a mixture, removing from the mixture water and excess phenol by distillation, and filtering off sodium bromide, said tetrabutylammonium phenolate and phenol being present in said formulation in a weight ratio of 40:60 to 70:30, said formulation having a solidification point of less than 25°C.

8. A process for preparing a formulation containing tetrabutylammonium phenolate and phenol comprising combining a solution of tetrabutylammonium bromide in phenol with a solution of sodium phenolate trihydrate in phenol to form a mixture, removing from the mixture water and excess phenol by distillation, and filtering off sodium bromide, said tetrabutylammonium phenolate and phenol being present in said formulation in a weight ratio of 40:60 to 70:30, said formulation having a solidification point of less than 25°C.

9. The formulation prepared by the process of Claim 6.

10. A method of using the formulation of Claim 9 comprising preparing a catalyst.

-7-

LIQUID TETRABUTYL AMMONIUM PHENOLATE FORMULATION

ABSTRACT OF THE DISCLOSURE

A process for preparing a formulation containing tetrabutylammonium phenolate and phenol is disclosed. The process entails combining a solution of tetrabutylammonium bromide in phenol with a solution of sodium phenolate to form a mixture, excess phenol is removed by distillation, and sodium bromide is filtered off. The formulation, that contains tetrabutylammonium phenolate and phenol in a weight ratio of 40:60 to 70:30, has a solidification point of less than 25°C. and finds use as a catalyst constituent.

WO 00/37402

LeR 33477

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231.

RECD PCTO 18 JUN 2001

Dorothy F. Colangelo

(Name of person mailing paper or fee)

Mary F. Colangelo

(Signature of person mailing paper or fee)

Liquid formulation of tetrabutylammonium phenolate

The present invention relates to a formulation of tetrabutylammonium phenolate that is liquid at room temperature, and to processes for its preparation.

5

Various tetraalkylammonium phenolates have already become known. For example, J. Am. Chem. Soc. 103 (1983) 475 and Inorg. Chem. 24 (1985) 3465 disclose the preparation of tetraethylammonium phenolate; the preparation of tetrabutylammonium phenolate is known from DE-OS 22 03 448; and EP-A 244 799 teaches the preparation of an electrolyte containing tetraalkylammonium phenolates.

10

Various phenol adducts of tetraalkylammonium phenolates have also already become known. J. Chem. Soc. Faraday Trans. 89 (1993) 119 discloses the preparation of (mono)phenol adducts of various tetraalkylammonium phenolates, and the preparation of the di(p-tert-butylphenol) adduct of tetrabutylammonium (p-tert-butylphenolate) is disclosed in EP-A 362 854.

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All those compounds are substances that are solid at room temperature. For large-scale application, however, it is desirable to have available a formulation that is liquid at room temperature, since metering is greatly simplified thereby.

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The invention provides formulations containing tetrabutylammonium phenolate (TBAP) and phenol in a weight ratio of from 40:60 to 70:30, preferably from 50:50 to 60:40, and having a solidification point of < 25°C, preferably < 20°C.

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The invention also provides processes for the preparation of the formulations according to the invention. The formulations according to the invention can be prepared by first dissolving sodium phenolate and tetrabutylammonium bromide (TBAB) separately at temperatures of > 40°C in phenol. When the two phases are brought together, sodium bromide is immediately formed as a fine precipitate.

- 2 -

Excess phenol is removed by distillation under reduced pressure until the desired mixing ratio of TBAP and phenol is achieved.

After cooling to room temperature, sodium bromide is separated off from the cloudy liquid. That can be effected by the conventional methods known to the person skilled in the art, for example by filtration, sedimentation or centrifugation. Separation of the precipitate is preferably carried out by filtration. In an especially preferred embodiment, the filtration is carried out over a pressure suction filter having a filter mat for finely dispersed materials (deep-bed filtration). The sodium content of the filtered solution is lower, the finer the filter used. If filter mats having retention rates of < 40 µm are used, formulations containing less than 1000 ppm sodium ions can be obtained.

Since sodium phenolate is relatively poorly soluble in phenol, a large excess of phenol must first be used, which must later be removed again. In a preferred embodiment of the process according to the invention, therefore, sodium phenolate is dissolved in a small amount of water and added to a solution of tetrabutylammonium bromide in phenol. The water is subsequently removed by distillation as an azeotropic mixture with phenol. In that variant, only about one tenth of the amount of phenol that is required for preparation *via* sodium phenolate solutions in phenol is required to prepare the formulations according to the invention. Moreover, the sodium contents of the resulting solutions are markedly lower, with values of < 500 ppm.

The formulations according to the invention are preferably used as a constituent of catalyst systems, for example for the production of phenol resins. Accordingly, the invention relates also to the use of the formulations according to the invention as a catalyst constituent.

Examples

5 Salts having a water content of < 500 ppm were used. The water content of the products was determined by means of Karl-Fischer titration, the bromide content was determined by argentometry, and the sodium content was determined by ICP.

Example 1

- In a 250 ml two-necked flask having a Vigreux column and a distillation bridge, a magnetic stirrer bead and a glass stopper, 36.8 g (0.11 mol) of TBAB were added to 10 36.8 g (0.39 mol) of molten phenol, and the mixture was allowed to cool to room temperature (solution A). In a 250 ml glass beaker, 19.4 g (0.11 mol) of sodium phenolate trihydrate were dissolved in 30 ml of water (solution B).
- 15 Solution A was then added dropwise to B in the course of 15 minutes at 60°C, with rapid stirring. Finally, 43 g of molten phenol were added. Approximately 64 g of that mixture were distilled off *in vacuo*. The residue consisted of a dark brown liquid with a fine beige-coloured sediment, which was filtered off over a pressure suction filter lined with a filter mat having a retention rate of 15-35 µm (T2100, Seitz 20 Filterwerke GmbH, D-55543 Bad Kreuznach).

The sodium content was 250 ppm, the bromide content was 0.21 wt.%.

Example 2

- 25 The procedure was analogous to Example 1, but a filter mat having a retention rate of 25-70 µm (T5500, Seitz Filterwerke GmbH, D-55543 Bad Kreuznach) was used for the filtration.
- 30 The sodium content was 1600 ppm, the bromide content was 0.38 wt.%.

Example 3

In a 1 litre three-necked flask, 19.4 g (0.11 mol) of sodium phenolate trihydrate were dissolved in 600 g (6.4 mol) of phenol (solution A). In a 100 ml glass beaker, 36.75 g (0.11 mol) of TBAB were dissolved in 36.75 g (0.39 mol) of phenol, while heating, and the mixture was then allowed to cool to room temperature (= solution B).

Solution B was added to solution A, and excess phenol was removed by distillation *in vacuo* at an internal temperature of 60°C until a molar ratio of TBAP:PhOH of approximately 1:8 was achieved. The sodium bromide that had formed was filtered off over a pressure suction filter with a filter mat having a retention rate of 15-35 µm (T2100, Seitz Filterwerke GmbH, D-55543 Bad Kreuznach).

15 The sodium content was 700 ppm, the bromide content was 0.21 wt.%.

Example 4

In a 1 litre three-necked flask, 19.4 g (0.11 mol) of sodium phenolate trihydrate were dissolved in 30 ml of water (solution A). In a 100 ml glass beaker, 36.75 g (0.11 mol) of TBAB were dissolved in 36.75 g (0.39 mol) of phenol, while heating, and the mixture was then allowed to cool to room temperature (= solution B).

Solution B was added to solution A, and water and excess phenol were removed by distillation *in vacuo* at an internal temperature of 60°C until a weight ratio of TBAP to phenol of approximately 1:1 was achieved. The sodium bromide that had formed was filtered off over a pressure suction filter with a filter mat having a retention rate of 15-35 µm (T2100, Seitz Filterwerke GmbH, D-55543 Bad Kreuznach).

- 5 -

The sodium content was 250 ppm, the bromide content was 0.21 wt.%, and the water content was 800 ppm.

Example 5

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Example 4 was repeated, but the reaction mixture was stirred at 60°C for 16 hours before being filtered.

10 The sodium content of the filtrate was 180 ppm, the bromide content was 0.18 wt.%, and the water content was 900 ppm.

Patent Claims:

1. Formulations containing tetrabutylammonium phenolate and phenol in a weight ratio of from 40:60 to 70:30 and having a solidification point of < 25°C.
5
2. Process for the preparation of the formulations according to claim 1, in which solutions of tetrabutylammonium bromide and sodium phenolate in phenol are combined, excess phenol is removed from the mixture by distillation, and
10 sodium bromide is then filtered off.
3. Process for the preparation of the formulations according to claim 1, in which a solution of tetrabutylammonium bromide in phenol and an aqueous solution of sodium phenolate are combined, water and excess phenol are removed from the mixture by distillation, and sodium bromide is then filtered off.
15
4. Process for the preparation of the formulations according to claim 1, in which solutions of tetrabutylammonium bromide and sodium phenolate trihydrate in phenol are combined, water and excess phenol are removed from the mixture by distillation, and sodium bromide is then filtered off.
20
5. Use of formulations according to claim 1 as a catalyst constituent.

COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

* As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

LIQUID TETRABUTYL AMMONIUM PHENOLATE FORMULATION

the specification of which is attached hereto,

or was filed on **December 9, 1999**

as a PCT Application Serial No. **PCT/EP99/09689**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 58 967.0
(Number)

Germany
(Country)

December 21, 1998
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Le A 33 477-US

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

- (12)
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